

19



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

11 Publication number:

**0 384 598  
A1**

12

## EUROPEAN PATENT APPLICATION

21 Application number: **90301102.1**

51 Int. Cl.<sup>5</sup>: **C09J 7/00, C09J 7/02,  
C08F 255/00, C08J 7/18**

22 Date of filing: **02.02.90**

30 Priority: **21.02.89 US 312458**

43 Date of publication of application:  
**29.08.90 Bulletin 90/35**

84 Designated Contracting States:  
**DE FR GB IT SE**

71 Applicant: **MINNESOTA MINING AND  
MANUFACTURING COMPANY**  
**3M Center, P.O. Box 33427**  
**St. Paul, Minnesota 55133(US)**

72 Inventor: **Johnson, Michael A., c/o Minnesota  
Mining and  
Manufacturing Co., 2501 Hudson Road,  
P.O.Box 33427**  
**St. Paul, Minnesota 55133-3427(US)**  
Inventor: **Harmon, Kimberly K., c/o Minnesota  
Mining and  
Manufacturing Co., 2501 Hudson Road,  
P.O.Box 33427**  
**St. Paul, Minnesota 55133-3427(US)**

74 Representative: **Baillie, Iain Cameron et al**  
**c/o Ladas & Parry Isartorplatz 5**  
**D-8000 München 2(DE)**

54 **Dual-functional adhesive tapes.**

57 Dual-functional adhesive tapes of the invention comprise a polyolefin heat-activatable adhesive, graft-polymerized to at least a portion of this adhesive, at least one monomer selected from the group consisting of acrylic acid, methacrylic acid and esters thereof; acrylamide; methacrylamide; sterically nonhindered tertiary alkyl acrylamides and methacrylamides; secondary alkyl acrylamides and methacrylamides having three or less carbon atoms in the alkyl group; and N-vinyl pyrrolidone, and firmly adherently bonded to the graft-polymerized monomer, an acrylic-type pressure-sensitive adhesive, wherein pressure-sensitive adhesive remains firmly bonded to the heat-activatable adhesive even when the tape is heated to permit attachment of the heat-activatable adhesive to a substrate.

**EP 0 384 598 A1**

## DUAL-FUNCTIONAL ADHESIVE TAPES

Field of the Invention

This invention relates to dual-functional adhesive tapes, more specifically to adhesive tapes comprising a layer of heat-activatable polyolefin adhesive having an acrylic pressure-sensitive adhesive adhered thereto.

Description of the Related Art

Pressure-sensitive adhesives are extremely popular for use in attachment tapes. Their use allows for fast, easy attachment of product components without the use of tools, messy liquid adhesives, or mechanical fasteners. They can be affixed by the average workman without a great deal of skill and experience. Pressure-sensitive adhesives tapes are available with a variety of properties depending on the particular application, e.g., type of substrate. Acrylic pressure-sensitive adhesives are widely popular as they are readily available and provide a good balance of tack, shear and peel properties on a variety of substrates at a relatively low cost.

Domestic and automotive weatherstrip seals and gaskets are commonly manufactured from materials such as ethylene-propylene-diene monomer and neoprene. These compositions are characterized as low surface energy elastomers. Such materials are difficult substrates for adhesives, particularly pressure-sensitive adhesives. Acrylic pressure-sensitive adhesives do not bond effectively to polyolefin substrates, in fact, polyolefin films are frequently used as release liners for acrylic adhesives. Various types of treatments to increase adhesion have been attempted, however, durability of the surface treatment has often been a problem. Use of a layer or coating of material which is a good substrate for the adhesive has also been attempted. However, the weak link in this system is the interface between the polyolefin and the coating.

U.S. Patent No. 4,563,388, (Bonk et al.) discloses an adhesive product in which the substrate is a polyolefin material and an acrylic type normally tacky and pressure-sensitive adhesive is bonded thereto by means of a graft-polymerized monomer coating. These adhesives are disclosed to remain bonded at temperatures up to 120° C.

Heat-activatable polyolefin adhesives, e.g., polyethylene, polypropylene, or polyallomer (an ethylene:propylene copolymer) are well known for use on polyolefin substrates. However, such adhesives do not provide the processing and application convenience of pressure-sensitive adhesives. Further, such adhesives do not yield high performance on all low-energy substrates.

It is particularly desirable for applications such as weatherstrip to have a dual-functional adhesive tape. A dual-functional tape has both a heat-activatable adhesive layer to bond to the polyolefin substrate, e.g., the weatherstripping, and a pressure-sensitive adhesive layer to supply the convenient quick bond to the substrate, e.g., a painted automobile door or other metal surface. However, this is even more difficult than bonding a non-adhesive polyolefin substrate. This is because the pressure-sensitive adhesive must remain adhered even when the heat-activatable adhesive softens, melts and flows, typically at temperatures of about 150° C and higher. It is further desirable to have a heat-activatable adhesive which has high adhesion to polyolefin substrates as well as to other low surface energy compositions.

U.S. Patent Nos. 4,101,210, and 4,130,535 (Coran et al.), disclose dynamically vulcanized thermoplastic elastomers comprising blends of high unsaturation diene rubber and thermoplastic olefin resin in which the rubber is cured. The elastomers are disclosed to have improved toughness and tensile strength. The rubbers are disclosed to be useful for making a variety of articles such as hoses, belts, gaskets, and other injection molded items. The use of such elastomers as adhesives is not disclosed.

U.S. Patent No. 4,350,740, discloses modified  $\alpha$ -monoolefin polymers with unsaturated carboxylic acid which give greater adhesion to metal when free-radical curing is done in the presence of N-maleamic acids or N-maleimide. Thermoplastic polymers are especially preferred, especially polypropylene, and copolymers of ethylene and propylene.

Applicants have now discovered that a dual-functional adhesive tape including a layer of a heat-activatable adhesive and a layer of a pressure-sensitive adhesive may be made by adhering the pressure-sensitive adhesive to a ionizing-radiation grafted primer layer coated onto the heat-activatable adhesive. The pressure-sensitive adhesive layer will remain adhered to the heat-activatable adhesive layer even when

such layer melts during attachment.

In preferred dual-functional adhesive tapes of the invention the heat-activatable adhesive comprises a dynamically vulcanized olefin.

5

### Summary of the Invention

Dual-functional adhesive tapes of the invention comprise a layer of heat-activatable adhesive and at least one layer of ultraviolet radiation-polymerized acrylic pressure-sensitive adhesive, wherein such pressure-sensitive adhesive layers are adhered to the heat-activatable adhesive layer by means of a high-energy radiation grafted primer layer.

In one preferred embodiment of dual-functional adhesive tape constructions of the invention, the pressure-sensitive adhesive layer is a foam or foam-like layer, and the tape further comprises a second nonfoam-like acrylic pressure-sensitive adhesive layer coated atop the foam-like adhesive layer.

Specifically, dual-functional adhesive tapes of the invention comprise a polyolefin heat-activatable adhesive having graft-polymerized to at least a portion thereof, at least one monomer selected from the group consisting of acrylic acid, methacrylic acid and esters thereof; acrylamide; methacrylamide; sterically unhindered tertiary alkyl acrylamides and methacrylamides; secondary alkyl acrylamides and methacrylamides having three or less carbon atoms in the alkyl group; and N-vinyl pyrrolidone, and firmly adherently bonded to the graft-polymerized monomer, an ultraviolet radiation-polymerized acrylic-type pressure-sensitive adhesive, wherein the pressure-sensitive adhesive remains firmly bonded to the heat-activatable adhesive even when the heat-activatable adhesive is softened during attachment.

In one preferred embodiment, the polyolefin heat-activatable adhesive comprises a dynamically vulcanized olefin adhesive. Such adhesives show exceptional adhesion to EPDM rubber when compared with adhesives of the prior art.

Also provided is a method for making dual-functional tapes of the invention comprising the steps of

- (a) extruding a heat-activatable adhesive,
  - (b) coating onto said heat-activatable adhesive a monomer composition selected from the group consisting of acrylic acid, methacrylic acid and esters thereof; acrylamide; methacrylamide; sterically unhindered tertiary alkyl acrylamides and methacrylamides; secondary alkyl acrylamides and methacrylamides having three or less carbon atoms in the alkyl group; and N-vinyl pyrrolidone,
  - (c) irradiating the coated heat-activatable adhesive with ionizing radiation to graft-polymerize said monomer to said heat-activatable polyolefin adhesive,
  - (d) applying a layer of acrylic type pressure-sensitive adhesive over the graft-polymerized monomer.
- All parts, percentages, and ratios herein are by weight unless otherwise specifically noted.

### Detailed Description of the Invention

40

Useful heat-activatable adhesives of dual-functional tapes of the invention are polyolefin homopolymers, such as polyethylene, polypropylene, derivatives thereof and copolymers thereof. Examples of copolymers include ethylene-acrylic acid copolymers having various ratios, polypropylene acrylic acid and polyethylene acrylic acid copolymers, and blends of polyethylene and ethylene vinyl acetate. The thickness of the polyolefin heat activatable adhesive layer is at least about 25 micrometers, preferably from about 75 micrometers to about 125 micrometers.

Useful heat-activatable adhesives include Primacor™ 3330, available from Dow Chemical, Polybond 1001, available from BP Performance Polymers, and dynamically vulcanized polyolefins available from Monsanto Chemical Company under the name Santoprene™, e.g., Santoprene™ 201-73. Preferred heat-activatable adhesives are Santoprene™ polyolefins, especially those having a Shore D hardness of about 50 or less, and a Shore A hardness of 55 or more.

Preferred heat-activatable adhesives of the invention effectively adhere to both thermoplastic and thermoset substrates. The adhesives achieve a high degree of compatible interfacial mixing with a thermoplastic substrate while molten, which upon cooling yields a high-strength bond. With a thermoset substrate, the molten adhesive achieves a superior wetting out of the substrate surface, again yielding a high strength bond when cooled.

The heat-activatable adhesives may contain fillers such as pigments, crosslinking agents, viscosity

agents, dispersants, and extrusion aids.

The monomers suitable for graft-polymerization onto the polyolefin heat-activatable adhesive to promote adherence of the pressure-sensitive adhesive thereto include acrylic acid, methacrylic acid and esters thereof; acrylamide; methacrylamide; sterically non-hindered tertiary alkyl acrylamides and methacrylamides; secondary alkyl acrylamides and methacrylamides having three or less carbon atoms in the alkyl group; and N-vinyl pyrrolidone.

Examples of useful esters of acrylic acid and methacrylic acid include hydroxyethyl methacrylate, isobutyl methacrylate, hexanediol diacrylate, n-hexyl methacrylate,  $\beta$ -carboxyethyl acrylate, thiodiethylene glycol diacrylate, glycidyl methacrylate, 2,3-dibromopropyl acrylate and diethylaminoethyl acrylate. Examples of useful sterically non-hindered tertiary alkyl acrylamides and methacrylamides include N,N-dimethyl acrylamide, N,N-diethyl acrylamide, N,N-dipropyl acrylamide, N-ethyl-N-butyl acrylamide, N,N-dimethyl methacrylamide, N,N-diethyl methacrylamide, and N,N-dipropyl methacrylamide. The preferred sterically non-hindered tertiary alkyl acrylamides include N,N-dimethyl acrylamide, N,N-diethyl acrylamide, and N,N-dipropyl acrylamide. Useful secondary alkyl acrylamides include N-methyl acrylamide, N-ethyl acrylamide, and N-n-propyl acrylamide.

Where quick bonding of the pressure-sensitive adhesive is desired, a composition comprising pure monomer is preferred. However, certain additional ingredients may be present in the monomer composition where properties such as internal strength or wet out are desirable. Crosslinking agents useful in monomer compositions include polyethylene glycol diacrylate, pentaerythritol tetraacrylate, tetraethylene glycol dimethacrylate, trimethylol propane triacrylate, trimethylol propane trimethacrylate, allyl methacrylate, 1,6-hexanediol diacrylate, thiodiethylene glycol diacrylate and triallyl cyanurate. Preferred crosslinking agents include polyethylene glycol diacrylate, tetraethylene glycol dimethacrylate, trimethylol propane triacrylate and 1,6-hexanedioldiacrylate. Crosslinking agent may be present in monomer compositions in amounts of from 0 to about 20 percent, preferably from 0 to about 10 percent.

The monomer composition contains about 80 to about 100 percent monomer, preferably from about 90 to about 100 percent monomer, when used with a crosslinking agent. The monomer compositions may also contain various additives such as wetting agents.

The thickness of the monomer compositions is preferably less than about 5 micrometers, preferably less than about 1 micrometer, and most preferably less than about 0.5 micrometer. It is believed that thickness approaching a single molecular layer would function effectively.

The monomer composition is graft-polymerized onto the heat-activatable adhesive composition by use of ionizing radiation such as actinic radiation, electron beam radiation, beta rays, gamma rays, x-rays, or use of a laser beam. Electron beam irradiation is preferred. Electron-beam dosage is typically greater than about 0.05 Mrads, preferably from about 0.5 Mrads to about 5 Mrads. The photopolymerized pressure-sensitive adhesive is then laminated onto the graft-polymerized composition.

The pressure-sensitive adhesive layer of dual-functional adhesive tapes of the invention comprises an ultraviolet-radiation polymerized acrylic pressure-sensitive adhesive. The acrylic adhesives useful for the pressure-sensitive adhesive layer of tapes of the invention preferably contain at least one alkyl acrylate monomer, preferably a monofunctional unsaturated acrylate ester of non-tertiary alkyl alcohol, the molecules of which have from about 4 to about 14 carbon atoms. Such monomers include, e.g., isooctyl acrylate, 2-ethyl hexyl acrylate, isononyl acrylate, decyl acrylate, dodecyl acrylate, butyl acrylate, and hexyl acrylate. The alkyl acrylate monomers can be used to form homopolymers for the photopolymerizable polymer or they can be copolymerized with polar copolymerizable monomers. When copolymerized with strongly polar copolymerizable monomers, the alkyl acrylate monomer generally comprises at least about 75% of the photopolymerizable polymers. When copolymerized with moderately polar copolymerizable monomers, the alkyl acrylate monomer generally comprises at least about 60% of the photopolymerizable polymer.

The polar copolymerizable monomers can be selected from strongly polar copolymerizable monomers such as acrylic acid, itaconic acid, hydroxyalkyl acrylates, cyanoalkyl acrylates, acrylamides or substituted acrylamides, or from moderately polar copolymerizable monomers such as N-vinyl pyrrolidone, acrylonitrile, vinyl chloride or diallyl phthalate. Where strongly polar monomers are used, they preferably comprise from about 1 parts to about 25 parts, preferably from about 4 to about 20 parts of the acrylic copolymer. Where moderately polar monomers are used, they preferably comprise from about 20 to about 40 parts of the acrylic copolymer.

The mixture of the polymerizable monomers also contains a photoinitiator to induce polymerization of the monomers. Photoinitiators which are useful include the benzoin ethers such as benzoin methyl ether or benzoin isopropyl ether, substituted benzoin ethers such as anisole methyl ether, substituted acetophenones such as 2,2-diethoxyacetophenone and 2,2-dimethoxy-2-phenylacetophenone, substituted alpha-ketols such as 2-methyl-2-hydroxypropionophenone, aromatic sulfonyl chlorides such as 2-naphthalene

sulfonyl chloride, and photoactive oximes such as 1-phenyl-1,1-propanedione-2-(o-ethoxycarbonyl)-oxime. The photoinitiator is present in an amount of about 0.01 to about 1 part per hundred parts of the acrylic monomers (phr) of the instant removable pressure-sensitive adhesive compositions.

The photopolymerizable monomer mixtures may also contain a crosslinking agent to enhance heat resistance. Preferred crosslinking agents for an acrylic pressure-sensitive adhesive are multifunctional acrylates such as 1,6-hexanediol diacrylate as well as those disclosed in U.S. Patent No. 4,379,201 (Heilmann et al.), such as trimethylolpropane triacrylate, pentaerythritol tetracrylate, 1,2-ethylene glycol diacrylate, and 1,2-dodecanediol diacrylate. Other useful crosslinking agents include the substituted triazines, such as those disclosed in U.S. Patent Nos. 4,329,384, 4,391,687, and 4,330,590 (Vesley), e.g., 2,4-bis(trichloromethyl)-6-(3,4 dimethoxyphenyl)-s-triazines and other chromophore halogen-s-triazines. When used, the crosslinking agent is present in an amount of from about 0.01 to about 1 phr.

In one preferred embodiment, the pressure-sensitive adhesive layer comprises an acrylic cellular pressure-sensitive adhesive membrane as described in U.S. Patent No. 4,415,615 (Esmay et al.).

A cellular pressure-sensitive adhesive membrane is made by the steps of

- (a) frothing a composition which is polymerizable to a pressure-sensitive adhesive state,
- (b) coating the froth onto a backing, and
- (c) polymerizing the coated froth in situ to a pressure-sensitive adhesive state to provide a pressure-sensitive adhesive membrane having a cellular structure.

Frothing can be conveniently accomplished by whipping a gas into the polymerizable composition. After coating the frothed composition onto a backing, the polymerization may be initiated by ultraviolet radiation as taught in U.S. Patent No. 4,181,752, (Martens et al.). Where such photopolymerization is desired, an inert frothing gas is preferably used as air tends to quench photopolymerization. Carbon dioxide and nitrogen are preferred frothing gases.

In another preferred embodiment, the pressure-sensitive adhesive layer may be a foam-like layer, e.g., a monomer blend comprising microspheres may be used. The microspheres may be glass or polymeric. The microspheres should have an average diameter of 10 to 200 micrometers, and comprise from about 5 to about 65 volume percent of the core layer. The thickness of foam-like layers in preferred tapes of the invention range from 0.3 mm to about 4.0 mm in thickness.

Preferred glass microspheres have average diameters of about 50 micrometers. When glass microspheres are used, the pressure-sensitive adhesive layer should be at least 3 times as thick as their diameter, preferably at least 7 times. The thickness of layers containing such glass microspheres should be at least six times, preferably at least twenty times that of each microsphere-free layer.

Polymeric microspheres are also useful for some compositions such as those described in U.S. Patent Nos. 3,615,972, 4,075,238, and 4,287,308, and 4,855,170. The microspheres are available from Kema Nord Plastics under the trade name "Expancel" and from Matsumoto Yushi Seiyaku under the trade name "Micropearl". In expanded form, the microspheres have a specific density of approximately 0.02-0.036 g/cc. It is possible to include the unexpanded microspheres in the core layer and subsequently heat them to cause expansion, but it is generally preferred to mix in the expanded microspheres. This process ensures that the hollow microspheres in the final core layer are substantially surrounded by at least a thin layer of adhesive.

In a highly preferred embodiment, the dual-functional tape comprises a second pressure-sensitive adhesive layer. Such second layer consists of a polymerized acrylic copolymer which may incorporate similar or dissimilar acrylic monomers in like or unlike thicknesses, having similar or different additives from those acrylic copolymers contained in the first adhesive layer. In such an embodiment, one layer is preferably a foam or foamlike acrylic adhesive; the second layer is a non-foam type acrylic adhesive.

Other useful materials which can be blended into the first or second pressure-sensitive adhesive layer include, but are not limited to, fillers, pigments, fibrous reinforcing agents, woven and nonwoven fabrics, foaming agents, antioxidants, stabilizers, fire retardants, and viscosity adjusting agents.

An especially useful filler material is hydrophobic silica as disclosed in U.S. Patents No. 4,710,536 and 4,749,590, (Klingen et al.). In one preferred embodiment of the present invention, the pressure-sensitive adhesive layer further comprises from about 2 to about 15 phr of a hydrophobic silica having a surface area of at least 10 m<sup>2</sup>/g.

The pressure-sensitive adhesive compositions of the invention are preferably prepared by premixing together the photopolymerizable monomers and the photoinitiator. This premix is then partially polymerized to a viscosity in the range of from about 500 cps to about 5,000 cps to achieve a coatable syrup. Alternatively, the monomers may be mixed with a thixotropic agent such as fumed hydrophilic silica to achieve a coatable thickness. The crosslinking agent(s) and any other ingredients are added to the syrup prior to in situ crosslinking and polymerization.

Method of Manufacture

A dual-functional tape of the invention is typically made according to the following procedure. A surface treated heat activatable olefin film is made by extruding a thermoplastic olefin elastomer from a single screw extruder onto a silicone coated polyester liner, followed immediately by orienting the film liner composite between a water cooled chrome roll and a rubber roll with the chrome roll touching the surface of the olefin film, to the appropriate thickness.

The surface of the olefin film is then coated with a monomer solution. The coating procedure involves application of the monomer composition in a manner which achieves a relatively uniform coating.

The coated surface is then exposed to electron beam radiation at a dosage of about 5 Mrads, a voltage of about 175 Kv in a nitrogen atmosphere, to result in the graft polymerization of the monomer coating.

A foam-like pressure-sensitive adhesive is made by partially polymerizing a mixture of 100 parts of a alkyl acrylate/polar monomer mixture also containing a photoinitiator under inert atmosphere to a coatable viscosity of 500-5000 CPS by ultra-violet lights. To this was then added additional photoinitiator, crosslinking agent, any fillers such as fumed silica, and glass microbubbles. The composition is then exposed to a bank of ultra-violet lamps at a total energy of 440 mj/cm<sup>2</sup>.

One face of this pressure-sensitive adhesive is then laminated to the primed surface of the heat-activatable adhesive to form the dual-functional tape.

Test Methods90° Peel Test

The tape to be tested was slit to a width of 1.27 mm and was then laminated to a substrate (the substrate can be a dynamically vulcanized olefin elastomeric film, made of Santoprene (R) 103-40 available from Monsanto, or EPDM rubber available from Cooper Rubber, both of approximately 2.54 cm wide and 0.32 cm thick) with its heat activatable surface bonded to the substrate. The lamination was accomplished using a "WL-30" laminator, available from 3M, operating at 150 volts and 150 cm/sec. and the composite was allowed to cool to room temperature. The pressure-sensitive adhesive coated surface of this composite was then adhered to a piece of anodized aluminum or a DCT 3000 painted panel of also 2.54 cm wide, available from PPG. Pressure was applied to insure good contact. The composite was then pulled at 90° angle away from the substrate. The peel force was recorded in N/dm and the failure mode was noted.

For samples of this invention, the peel test resulted in cohesive failure of the foam-like adhesive, indicating that the interfacial strengths of the heat activatable olefinic film to both the substrate and the pressure sensitive foam-like adhesive were greater than the cohesive strength of the foam-like adhesive.

In some instances, the bonded constructions were first exposed to water immersion and/or salt spray prior to the peel adhesion measurement.

Environmental Cycling Test

The test consisted of subjecting the samples to a cycle of 8 hours at 88° C, followed by 16 hours at -40° C, 8 hours at 38° C and 100% Relative Humidity (RH), and finally for 16 hours at -40° C. This whole procedure was then repeated for 4 more cycles for a complete test.

180° Static Peel Test

This test was used to evaluate the elevated temperature performance of the interfacial strength of the tape composite under conditions of stress when stress was applied directly to the primed interface. The tape was first slit to a width of 1.27 cm and 20 cm length and then laminated by its heat activatable side to

a 20 cm long substrate made of Santoprene (R) 103-40 available from Monsanto. With a razor blade, the tape was nicked, through the adhesive surface about 10 cm from each end, penetrating through the tape into the substrate. The pressure-sensitive side was bonded to a painted panel (DCT-3000) using 2 passes of a 7 Kg roller. The assembly was allowed to dwell for 72 hours at room temperature prior to attaching a 250 gram weight to the free end of the assembly and bending the tape 180° to fold upon itself. It was then placed in an oven at a pre-set temperature for 30 minutes. After removal from the oven, the sample was allowed to cool and the failure mode was noted.

The following examples are for illustrative purposes only, and are not to be construed as limiting the invention. The scope of the invention is that defined by the claims.

## EXAMPLES

### Example 1

Heat-activatable adhesive priming process and article.

A surface treated heat activatable olefin film was made by first extruding a dynamically vulcanized thermoplastic olefin elastomer, available as Santoprene™ 201-80 - Shore A scale Hardness of 80 from Monsanto Company, from a single screw Haake extruder at a temp. of 220° C onto a silicone coated polyester liner, followed immediately by orienting the film liner composite between a water cooled chrome roll and a rubber roll with the chrome roll touching the surface of the olefin film, to a thickness of 0.063 mm.

The surface of the olefin film was then coated with a monomer solution containing 100 parts of N,N-dimethyl acrylamide and 0.1 parts of a fluorochemical acrylate oligomer, (a surfactant available from 3M as "FC 430"). The coating procedure involved saturating a Kim-wipe with the monomer solution and then wiping the clean surface of the olefin film with the solution, to achieve a relatively uniform coating of about 15 micrometers thick.

The coated surface was then exposed to electron beam radiation at a dosage of about 5 Mrads a voltage of about 175 Kv in a nitrogen atmosphere, and a line speed of 7.5 m/min. to result in the graft polymerization of the monomer coating.

### Example 2

A foam-like adhesive was made by partially polymerizing a mixture of 100 parts of a 87.5/12.5 isooctyl acrylate/acrylic acid (IOA/AA) and 0.03 parts Irgacure 651 (IRG), available from Ciba Geigy, under inert atmosphere to a coatable viscosity of 500-5000 CPS by ultra-violet lights. To this was then added an additional 0.1 parts IRG 651, 0.055 parts of 1,6-Hexanedioldiacrylate, 2 parts of fumed silica, Aerosil™ R972 available from Degussa, and 8 parts of C-15/250 glass microbubbles available from 3M. The composition was then frothed with nitrogen in a procedure similar to that described in U.S. 4,415,615, Esmay et al., to a density of 1024 Kg/m<sup>3</sup> and a final thickness of 1.0 mm. This was then exposed to a bank of ultra-violet lamps at a total energy of 440 mj/cm<sup>2</sup>. One face of this foam-like adhesive was then laminated to the primed surface of the film of Example 1 at a laminating temperature of 120° C to accelerated the bonding process, while the other face was laminated to a solvent-based adhesive transfer tape having a composition of isooctyl acrylate/methyl acrylate/acrylic acid (57.5/35 17.5) to form a composite. This tape composite was then tested according to the tests described above and results are shown in Table 1.

### Example 2-C<sub>1</sub>, 2-C<sub>2</sub>

These were made similar to Example 2, except that no surface treatment was performed for 2-C<sub>1</sub>, and 2-C<sub>2</sub> was exposed to E-beam without a coating of monomer grafting solution. These were also tested and were found not to have any anchorage between the heat-activatable adhesive film and the foam-like adhesive.

Examples 3-5, 3-C

These were made similar to Examples 1 and 2 except that a different primer was grafted. These differences are shown in Table 2. These tapes were also tested according to Example 2 and the results are shown in Table 1.

Examples 3 and 3-C were also tested on two other substrates: Cooper EPDM and Santoprene. These results are shown in Table 3.

TABLE 1

Examples	2	3	4	5
90° peel (N/dm)				
EPDM				
a) Room Temperature				
1 hr	137*	126*	147*	133*
72 hr	194*	207*	203*	214*
b) 88° C				
2 weeks	521**	425**	509**	
502**				
c) 100° C/100% RH				
72 hr	260*	306*	228*	277*
2 wks	285*	316*	309*	277*
d) Water Immersion				
240 hours	278*	197*	172*	270*
e) Salt Spray				
240 hours	341*	309**	277*	352*
f) Environmental Test				
Painted Panel				
434**	405**	376**	424**	
180° C Static Peel				
Anodized Aluminum				
a) 100° C */graft	*	*	*	
b) 110° C graft	no fail	no fail	no fail	
c) 120° C	***	***	***	***

\* sample peeled off the painted panel

\*\* cohesive failure of foam-like adhesive

\*\*\* pressure-sensitive adhesive separated from the foam-like adhesive graft  
foam-like adhesive separated from grafted interface

TABLE 2

Examples	Primer
3	100 % Glycidyl Methacrylate (GMA)
4	80/20 Glycidyl Methacrylate (GMA)/Trimethylol propane triacrylate(TMPTA)
5	80/20 N, N-dimethyl Acrylamide(DMA)/Trimethylol propane triacrylate(TMPTA)
3-C	Thermoplastic polyamide * (no grafting)

\* available as Macromelt 6240 by Henkel



TABLE 3

Examples	3	3	3-C
Substrate	Santoprene	Cooper EPDM	Santoprene
90° peel(N/dm)			
a) Rm. Temp. 1 hr	126*	108*	10.8**
72 hrs	154*	207*	11.6**
b) 88° C 2 wks.	529**	424**	1.8**
c) 100° C/100% RH 72 hrs.	291*	305*	144**
2 wks.	291*	315*	25**
d) Water Immersion 240 hrs.	273**	196*	91**
e) Salt Spray 240 hrs.	319*	308**	3**
f) Environmental Cycling Test	494**	375**	23**
180° Static Peel			
a) 100° C	*	*	
b) 110° C	no fail	--	
c) 120° C	***	*	

\* sample peeled off the substrate

\*\* adhesive failure of the foam-like adhesive

\*\*\* pressure-sensitive adhesive separated from the foam-like adhesive

Example 6

This was made similar to Examples 1 and 2 except a thermoplastic copolymer of ethylene and acrylic acid available as Primacor™ 3330 from Dow Chemical was used to produce the heat activatable film at a thickness of .08 mm and the film was corona treated prior to application of the grafting monomer. This was tested in a similar manner as Example 2 and the results are shown in Table 4.

Example 6-C

This was made similar to Example 3-C except the heat-activatable film was made from Primacor™ 3330. This was also tested in the same manner as Example 3-C and the results are shown also in Table 4.

TABLE 4

Examples	6	6-C
90 ° peel (N/dm)		
a) 88 ° C/100% RH 2 wks.	371**	304**
b) 100 ° C/100% RH 3 days	259**	208**
2 wks.	239**	218**
c) Water Immersion 10 days Rm Temp.	208**	208**
d) Salt Spray 10 days Rm Temp.	246**	224**
e) Environmental Cycling Test	272**	240**
180 ° Static Peel		
a) 100 ° C	no failure	*
b) 110 ° C	no failure	*

\*adhesive failure between polyamide film and ethylene acrylic film

\*\*adhesive failure of foam-like adhesive

#### Examples 7-10

These were made similar to Examples 1 and 2 except the Santoprene heat activatable film adhesive was replaced with 0.125 mm films made from two blends of polypropylene and EPDM, both of which are available from B P Performance Polymers, Inc., and different primers were grafted. These compositions of the blends and primers are shown in Table 5 and the test results are shown in Table 6.

TABLE 5

Examples	Primer	Polypropylene/EPDM ratio	Fillers
		(parts)	(parts)
7	100% dimethylacrylamide (DMA)	40/30	30
8	100% glycidyl methacrylate (GMA)	40/30	30
9	100% dimethylacrylamide (DMA)	40/60	small amount
10	100% glycidyl methacrylate (GMA)	40/60	small amount

TABLE 6

Example	7	8	9	10
Substrate	Santoprene	Santoprene	Santoprene	Santoprene
90° peel(N/dm)				
a)Room Temp				
1 hr.	394**	355**	380**	380**
72 hrs	394**	355**	380**	380**
b)88° C/100% RH				
24 hrs	424**	409**	426**	432**
14 days	360**	307**	439**	465**
c)34° C/100% RH				
14 days	236**	251**	255**	242**
d)Water Immersion				
10 days	276**	274**	275**	257**
e)Salt Spray				
10 days	256**	284**	260**	264**
f)Environmental Cycling Test	331**	340**	339**	325**

\*\* cohesive failure of foam-like adhesive

## Claims

1. A dual-functional adhesive tape comprising a layer containing a polyolefin heat-activatable adhesive having graft-polymerized by ionizing radiation to at least a portion thereof, at least one monomer selected from the group consisting of acrylic acid, methacrylic acid and esters thereof; acrylamide; methacrylamide; sterically nonhindered tertiary alkyl acrylamides and methacrylamides; secondary alkyl acrylamides and methacrylamides having three or less carbon atoms in the alkyl group; and N-vinyl pyrrolidone, and firmly adherently bonded to said graft-polymerized monomer, a layer containing an ultraviolet-radiation polymerized acrylic-type pressure-sensitive adhesive, wherein said pressure-sensitive adhesive remains firmly bonded to said heat-activatable adhesive even when said tape is heated for attachment.
2. The dual-functional adhesive tape of claim 1 wherein said graft-polymerized monomer is N,N-dimethylacrylamide.
3. The dual-functional adhesive tape of claim 1 wherein said heat-activatable adhesive is a dynamically vulcanized polyolefin.
4. The dual-functional adhesive tape of claim 1 wherein said acrylic-type adhesive comprises
  - (a) at least about 60 parts of an alkyl acrylate monomer, the alkyl groups of which have an average of 4 to 12 carbon atoms, and
  - (b) correspondingly, up to about 40 parts of a monoethylenically unsaturated polar copolymerizable monomer, and
  - (c) from about 0.01 part to about 10 parts of a photoinitiator per 100 parts of monomer.
5. The dual-functional tape of claim 4 wherein said acrylic-type adhesive comprises from about 60 to about 99 parts of an alkyl acrylate monomer selected from the group consisting of isooctyl acrylate, butyl acrylate, isononyl acrylate, 2-ethylhexyl acrylate, and isodecyl acrylate and correspondingly, from about 1 part to about 40 parts of a polar copolymerizable monomer, and where said polar copolymerizable monomer is selected from the group consisting of acrylic acid, itaconic acid, N-vinyl pyrrolidone, N-vinyl caprolactam, acrylamide, substituted acrylamide, and methacrylic acid.
6. The dual-functional tape of claim 5 wherein said acrylic-type adhesive further comprises microspheres selected from the group consisting of glass microspheres, and polymeric microspheres.
7. The dual-functional tape of claim 5 wherein said acrylic-type adhesive is a cellular pressure-sensitive adhesive.
8. The dual-functional tape of claim 5 further comprising a second layer of acrylic-type pressure-sensitive adhesive.

9. A method of making the dual-functional tape of claim 1 comprising the steps of

(a) extruding a heat-activatable adhesive,

(b) coating onto said heat-activatable adhesive a monomer composition selected from the group consisting of acrylic acid, methacrylic acid and esters thereof; acrylamide; methacrylamide; sterically  
5 nonhindered tertiary alkyl acrylamides and methacrylamides; secondary alkyl acrylamides and methacrylamides having three or less carbon atoms in the alkyl group; and N-vinyl pyrrolidone,

(c) irradiating the coated heat-activatable adhesive with ionizing radiation selected from actinic radiation or electron beam radiation to graft-polymerize said monomer to said heat-activatable polyolefin adhesive,

10 (d) applying a layer of acrylic type pressure-sensitive adhesive over the graft-polymerized monomer.

15

20

25

30

35

40

45

50

55



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 90 30 1102

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A, D	EP-A-0 120 708 (3M) ----		C 09 J 7/00
A	US-A-4 049 483 (H.A. LODER) -----		C 09 J 7/02
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 29-05-1990	Examiner BUSCAGLIONE Y.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			